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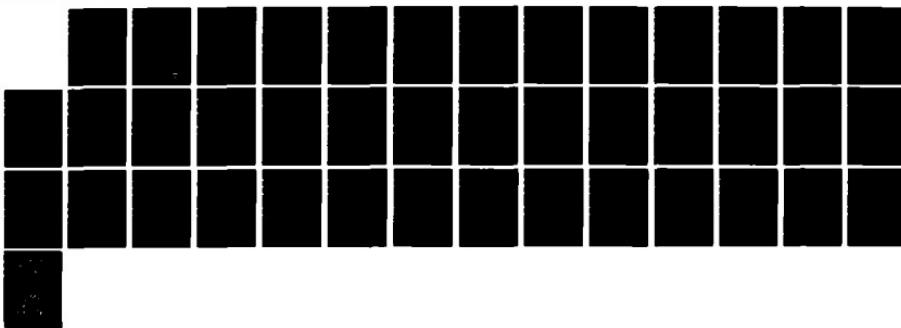
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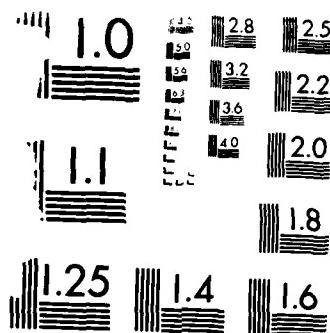
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TRACE ELEMENTS AND THEIR ASSOCIATIONS  
IN SEDIMENTS OVER THE HAMPTONROADS HARBOR  
AND LOWER CHESAPEAKE BAY AREA

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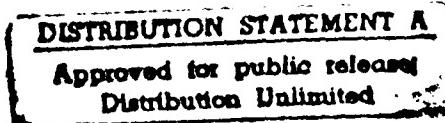


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Joseph H. Rule

July 1984



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Report B- 18

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## ABSTRACT

Acid extractable Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined on sediments from the Inner Virginia Shelf, and from shipping channels in the lower Chesapeake Bay and Hampton Roads Harbor system. Levels of Cd, Cu, Pb, and Zn exceeded average crustal abundances for most of the study sites. Cumulative frequency curves suggested that there were two major populations for all metals and perhaps a third and smaller one for Cd, Cr, and Mn. Plots of metal vs Fe indicated no anthropogenic inputs of metals for shelf and Chesapeake Bay channel sites, but suggested anthropogenic influences for all metals in several of the inshore sites. Enrichment factor calculations showed enrichment of Cd, Cu, Pb, and Zn with respect to average crustal abundances. A recommendation of this study for evaluation of environmental geochemical metals data is to utilize mean concentrations, cumulative frequency plots, and metal vs Fe and/or enrichment factor calculations when evaluating the pollution status of sediments.

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TRACE ELEMENTS AND THEIR ASSOCIATIONS  
IN SEDIMENTS OVER THE HAMPTON ROADS HARBOR  
AND LOWER CHESAPEAKE BAY AREA

Introduction

When assessing metal sediment concentrations for environmental studies, one major problem is the choice of methods of data analyses. One may attempt to evaluate the data based on absolute metal concentrations, or choose between a variety of other methods, ranging from relatively simple ones like elemental ratios to more sophisticated ones such as discriminant analysis.

Helz et al. (1983) analyzed sediments from the Chesapeake Bay, Baltimore Harbor, and Elizabeth River for trace elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb). They calculated enrichment factors (E.F.) for their data using Al as the reference metal and average crustal shale values from Turekian and Wedepohl (1961) by the relation:

$$EF = \frac{(X/Al) \text{ sediment}}{(X/Al) \text{ Earth's Crust}}$$

where X/Al is the ratio of the concentration of element X to Al. They found, in general, enrichment of Cd, Pb, and Zn in the Bay and postulated that this resulted from: (1) atmospheric deposition, or (2) unrepresentative crustal abundance data - perhaps metal concentrations in Chesapeake Bay are anomalous as compared to the average crustal abundances.

Using Fe based enrichment factors, Helz et al. (1983) compared their data to that from several other East and Gulf Coast estuaries and found enrichment of Cd, Pb, and Zn in most cases. They stated that the Al concentrations in both the Hampton Roads and Baltimore Harbor sediments were high when compared to the respective main Bay areas. In Hampton Roads, no consistent anthropogenic effect was found for Cr or V but Zn was highly enriched.

Goldberg et al. (1978) collected and analyzed eight cores from the Chesapeake Bay (including one from the James River). They presented detailed metal concentrations for four of these cores and concluded, from the absolute concentrations, that surface metal contents were considerably enriched over values below 50 cm. This trend was not clearly evident in all cases. In some instances, other types of data analysis may have provided a clearer indication of whether or not there was enrichment. Normalization of the trace metal concentrations to either Al or Fe may have been very useful for this purpose.

Sommer and Pyzik (1974) used metal versus aluminum/metal ratios as an aid to evaluate metal-sediment associations of Chesapeake Bay sediments. They determined that Al was associated with clay minerals in Bay sediment and used Al as an indicator of clay minerals. Linear relationships were found between Cu and Al/Cu; Pb and Al/Pb; Cr and Al/Cr; Mn and Al/Mn. Iron did not show a linear relationship. Sommer and Pyzik suggested that because of the linear relationships for Al and Cu, Pb, Cr, and Mn, these elements were associated with the clay mineral portion of the sediment and that an alternate distribution mechanism (sulfides) was possible for Fe.

Johnson and Villa, Jr. (1976) determined acid extractable metals in Elizabeth River sediments. They found that concentrations of all metals analyzed (Cd, Cu, Cr, Hg, Pb, Zn, Al, and Fe) were two to ten times greater than for sediments from the mid-Chesapeake Bay. Distribution of metals generally reflected heavy industrial, commercial, and domestic inputs along the river. Their findings are reviewed in the discussion section.

Johnson and Villa, Jr. (1976) discussed the work of Sommer and Pyzik (1974) and examined their data for metals in Elizabeth River sediments by the same metal vs Al/metal technique. No linear relationships were found for Fe, Cr, Pb, or Cu with Al. They then concluded that either Al was not associated with clay minerals in the Elizabeth River as it was in the Bay sediments, or non-linear relationships are indicative of anthropogenic sources rather than natural ones.

It seems highly unlikely that the association of Al with clay minerals (assuming these authors mean silicate clay minerals) would vary as postulated above, since Al is an inherent and abundant component of the clay minerals structure. Other forms of Al were undoubtedly present in sediments since the extraction techniques used by these workers would not significantly dissolve the silicate lattice. Whether or not these other forms of Al would be associated with silicate clay minerals may be questionable, but it is expected that these forms will be in the clay-sized fraction of sediments. Most of the Fe in sediments will be in the forms of hydroxides or sulfides, depending on Eh, and in the clay-size fraction. The most relevant conclusion as to the association and distribution of Al and Fe, with respect to clay minerals, is that the forms of all three occur predominantly

in the clay-sized sediment fraction. Many sediment forms of Al and Fe are relatively easily extracted; silicate clays are not.

Trefry and Presley (1976a, b) used metal vs Fe plots to characterize unpolluted sediments and to identify sediments thought to be polluted from anthropogenic sources. They did not use metal vs metal/Fe ratios but simple metal vs Fe scatter plots. A population that occurred within the +95% prediction interval about the best fit linear line was defined as natural or unpolluted. Metal concentrations occurring outside of the 95% interval were postulated to indicate anthropogenic input. Rule (1982) discussed sediment metals in the lower Chesapeake Bay and Hampton Roads Harbor area as evaluated by the technique of Trefrey and Presley.

Chester and Voutsinou (1981) used dilute HCl to extract sediment metals and assessed the sediment's pollution status by examining absolute trace metal concentrations. They suggest that spatial contour maps of surface metal concentrations are a simple and effective manner to present results. Although proposing the use of this simple method, they point out that great care is necessary in choosing baseline metal levels.

Absolute amounts of trace elements are, to some degree, simply a function of sediment particle size. Therefore, assessing a group of data where sediment particle size is variable must be done with caution. Even when the grain size is nearly homogeneous within a data set, the choice of baseline data must be done with care.

Sinex and Helz (1981) noted that certain unfractionated samples from the Chesapeake Bay contained higher trace element concentration than corresponding <63 $\mu$ m fractions. They postulated that the coarser grained

fraction contained fecal pellets, heavy minerals, aggregates of fine-grained materials, or sand grains with unusually thick coatings.

Shrader, Rule, and Furbish (1977) studied the distribution of several metals in different size fractions of stream sediments. They found that the concentration of some metals, notably Mn, was greater in the sand and clay fractions than in the silt sizes with the highest concentrations often in the sand sizes. This phenomenon is most probably attributable to Mn-oxide coatings on the sand grains.

Generally, the sediment fraction that contains the greatest concentrations of trace metal is, of course, the finer size. A very desirable method of assessing the trace metal status of sediments would be to analyze the  $<63\mu\text{m}$  material. In this manner, the variable effect of grain size will be eliminated. Most environmental studies utilize an unfractionated or  $<2\text{mm}$  portion of sediments for the various determinations. Analyses of the  $<63\mu\text{m}$  fraction, while desirable, would entail additional time and labor often beyond that available for the research. The most useful technique should allow use of chemical data from unfractionated samples, be applicable to a wide range of sediment types, and minimize the difficulty in selection of baseline or reference concentrations. A number of such techniques do exist; this paper evaluates some of them utilizing sediment metal data from the lower Chesapeake Bay, Inner Virginia Shelf, and Hampton Roads Harbor System. A suggested plan for the data analyses of trace metals in sediments is given.

### Materials and Methods

The Port of Hampton Roads, Virginia, is located within a major metropolitan area encompassed by Norfolk, Virginia Beach, Chesapeake, Portsmouth, Newport News, and Hampton (Figure 1). Waters of this harbor are along one of the most industrialized coastal areas in the eastern part of the United States. The largest military port in the world is located here. Navigation channels of this port system are maintained by the U.S. Army Corps of Engineers (COE). The COE dredges an annual average of 4.1 million m<sup>3</sup> of sediment from the port systems channels. Approximately 60% of this material is classified as mud, clay, and silt and is taken primarily from the Hampton Roads/Elizabeth River portion. These are the most active industrial areas in the port system. The balance of the dredged materials consists of sand, gravel, and shell which comes from the Chesapeake Bay Channels (Pequegnat *et al.*, 1978, current research).

The large Naval Base is located adjacent to Sites E and F; Sites G-I are on the main stem of the Elizabeth River where there is moderate industrial activity (fuel facilities and chemical companies). The highly industrialized area, with private and naval shipyards, oil storage and creosoting facilities, and fertilizer companies occur along Sites K, L, and M. A less densely developed area in the upper reaches of the Elizabeth River are represented by Sites P, Q, S, T.

Sediments from the highly industrialized segments are presently disposed at Craney Island, a diked disposal area (Figure 1). With normal maintenance, dredging and disposal operations, the Craney Island site will be available for several years but has a finite lifetime. Plans are also being made to

deepen the Port of Hampton Roads from the present 13.8m depth to 17m to accommodate deeper draft vessels. Should the deepening occur, the filling of Craney Island would be greatly accelerated. A multidisciplinary study was designed to investigate if open ocean disposal of sediments from various areas within the port system would be ecologically acceptable.

Sediment samples were collected to use in various types of bioassays, for particle size analyses, and for metals analysis. Sediment samples collected for all these various purposes were analyzed for trace metals.

One hundred and seventy-nine sediment samples were collected over a three-year period from forty-six stations in the navigation channels in the lower Chesapeake Bay (Thimble Shoal and Cape Henry channels), Hampton Roads Harbor, and the Elizabeth River (main stem and Southern Branch). Samples from a proposed offshore disposal site on the Inner Virginian Shelf about 27 km from the Bay mouth were also taken (included in the 179 count).

The sampling pattern for the offshore area is shown in Figure 1. All other samples, in the navigation channels, were taken at one-mile intervals using navigation buoys as site markers. At each site, four samples were taken across the channel between the buoys.

Sediment samples were collected using either a Shipek grab or a  $0.76\text{m}^3$  clamshell grab. Care was taken to avoid contamination from the samplers and the samples were placed in plastic bags for transport to the laboratory. Sediments were dried at  $<40^\circ\text{C}$ , crushed and passed through a 2mm stainless steel sieve and stored in plastic bags. Sediment grain-size analysis was performed on the samples collected from the Chesapeake Bay channels and the

offshore site as a part of the contracted study. Analysis of grain-size of the Hampton Roads and Elizabeth River samples were conducted where time permitted. Portions (2-6g) of the <2mm samples were extracted as follows: fifteen ml of concentrated (15.4 M) HNO<sub>3</sub> (redistilled) were added to the samples and then heated at 100°C for four hours. Five ml of 30% H<sub>2</sub>O<sub>2</sub> were added and the mixtures heated for an additional 2 hours. The extract was filtered through acid washed Whatman No.2 filter paper and diluted with ultrapure deionized water to a final acid concentration of 10%. The metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined by flame Atomic Absorption Spectrophotometry using a Perkin-Elmer 603 instrument. All data were calculated on a dry weight basis. Statistical calculations were conducted using the Statistical Packages for Social Sciences (SPSS) by Nie et al. (1975).

### Results and Discussion

Sediment metal concentrations as averaged for different areas are shown in Table 1. The areas are defined by site groupings in Table 2. Metal concentrations are generally lowest in the Norfolk Disposal Site (NDS) area. Except for Pb, concentrations of metals are similar for the NDS area and Outer Thimble Channel. The Inner Thimble Channel sediments, closer to inshore activities, have a slight but consistent increase in concentrations for all metals. The NDS sediments are fine sands; the Thimble Channel sediments range from coarse sands to fine material which is responsible for some of the increase in sediment metal concentrations.

Starting in the Inner Thimble Shoal Channel, the general pattern shows an increase in metal concentrations toward the industrialized portions of the Elizabeth River. Levels of Cd, Cu, Pb, and Zn exceeded average crustal abundances (Taylor, 1964, Table 3) in several sites close to industrial activities. Concentrations of Cd and Pb showed the greatest elevations above crustal abundances ( $>10X$ ) and this increase occurred for a greater number of sites than for other metals.

Maximum concentrations of Cd, Cr, Cu, and Pb occurred in sediments from the most highly industrialized area in the mid-Elizabeth River, while maximum values for Fe and Zn were found in the lower Elizabeth River. The highest values for both Mn and Ni occurred in the inner Hampton Roads sediments. The concentration pattern (Table 1) of Mn and Ni, and to a lesser extent, Mn and Co, suggests a geochemical association between these elements in the sediments. Geochemical association of Mn with Ni and Co has frequently been reported (Siegel, 1974; Levinson, 1980).

Concentrations of all metals decrease in the Uppermost Elizabeth River, reflecting the lower level of industrialization, but values in these sediments were still greater than those in the Thimble Shoal Channel and NDS area, and exceeded the average crustal abundance for Cd, Cu, Pb, and Zn.

Although there were no statistically significant differences in average concentrations of trace elements extracted from Elizabeth River sediments during the present study (sampled in 1979) and the levels measured by Johnson and Villa, Jr., 1976 (sampled in 1974, Table 4), the ranges for most metals for the present study were much more narrow than for that of Johnson and Villa, Jr. A more severe extraction procedure was used in the current study and the higher mean values may have resulted from the removal of a greater amount of metals from the sediments. Although the average Johnson and Villa, Jr.'s values were lower, there were several instances where maximum-found values exceeded those for the present study. This may have resulted from slightly different sampling patterns or may indicate a change in the distribution pattern of the metals.

There is, of course, a variation in grain size (Table 2) over the study area which causes some of the differences in trace metal levels; however, variations in metal concentrations also exist in similar grain-sized samples (such as in the Elizabeth River). Such observations are common in geochemical studies. Analyzing the  $<63\mu\text{m}$  fraction of sediments may help to resolve this problem. Since it was not possible in the current study to analyze the  $<63\mu\text{m}$  fraction, the next best approach was to use a method of data analysis which might account for grain-size effect. If a data assessment technique can be utilized which inherently incorporates the influence

(effect) of grain-size on the trace metal content, then there would be no need to group the data by particle size and a larger set of data can be compared.

Cumulative frequency plots of metal concentrations have long been used (Siegel, 1974) to determine the number of populations present in a group of samples. When a cumulative frequency curve for a given metal (metal concentration vs number of occurrences for each concentration) is constructed on a probability plot, a single population is defined as a group of points which form a straight line. Multiple populations within a single (given) data set will give two or more straight-line segments on the graph.

Cumulative frequency plots were constructed for each metal analyzed utilizing the entire data set. All curves had two distinct straight-line portions indicating two major populations present. Plots for Cd, Cu, Cr, and Mn (Figures 2 and 3) show the variety of curves obtained. The population defined by the near-vertical segment (low metal concentrations) includes the Norfolk Disposal Site and Thimble Shoal Channel sediments. The nearly horizontal segment (higher range of concentrations) includes the Hampton Roads Harbor and Elizabeth River sediments. The portion of the curves for Cd, Cr, and Mn between the larger near-vertical and near-horizontal segments may indicate that a third population is present.

The data were then divided into three groups based on geographic areas, sedimentological and geochemical characteristics, and cumulative frequency curves. The three groups were Norfolk Disposal Site (OFFSHORE); Thimble Shoal Channel (CHANNEL); and sites from the Hampton Roads Harbor and Elizabeth River (INSHORE).

It is assumed that for natural sediment conditions (no anomalous metal concentrations), the relationship between Fe and another metal will form a linear trend (Trefrey and Presley, 1976a, b). Should the concentration of Fe change because of changing mineralogy, sediment particle size (which will inherently change mineralogy) or other naturally occurring phenomena, the concentration of the other metal will change with a constant relation to Fe. If a scatterplot of metal vs Fe is constructed and a regression line with a 95% prediction band is plotted, then the natural geochemical population of a given data set is defined. That means there is a 95% probability that the points that fall within the prediction interval belong to the normal population and those that are outside of this band are from a different (or anomalous) population.

Metal/Fe plots were constructed for the OFFSHORE, CHANNEL, and INSHORE data groups and also for all data for each metal. Representative plots are shown in Figure 4.

Even though the metal concentrations vary greatly between the data sets in Figure 4, the same scale was used for comparative purposes. Correct plotting of OFFSHORE Cu for evaluation as a single data set is shown in Figure 5a. The slope and nature of the curves for the OFFSHORE and CHANNEL samples (Figure 4a,b) are very similar and no doubt from an unpolluted environment. Metal concentrations are low and all points fall within the 95% prediction interval.

When all sites of two data sets belong to the same population, they will fall along the same line of the metal/Fe curves. Those samples having coarser sediments with low metal concentrations will lie on the lower

portion near the ordinate; those samples having finer sediments with resulting higher metal concentrations will lie further to the right but along the same line. It is clear (Table 1) that the Thimble Channel sediments vary in metal content. The outer channel sites are generally more similar to the OFFSHORE than those in the inner channel. However, the OFFSHORE and CHANNEL samples form one population for Cu and if plotted together would fall along the same line. When samples are from different geochemical populations and have different metal/Fe ratios, they tend to form lines of different slopes when plotted on the same graph. The Cr/Fe plot in Figure 5b is a very good example of what appears to be two populations in one data set. The upper group of samples to the left fits closely with the points for a similar OFFSHORE plot (Figure 5c) while the other points lie along a distinctly different curve. The OFFSHORE and CHANNEL data for Cr/Fe horizontal row of points are from relatively coarse, clean sands in the Thimble Shoal Channel; they have very low and similar Cr concentrations.

The data distribution for the INSHORE sediment plots (Figure 4c) is totally different than for the other two groups. The points are widely scattered and the 95% prediction interval is relatively wide. Even so, several points are above this band, indicating anomalously high values. Although there is some particle-size variation in the INSHORE group, sediments are predominantly silt-sized or less. The anomalously high values are from sites along the highly industrialized portion of the Elizabeth River.

Each of the metal/Fe (Cu/Fe) plots in Figure 4a, b, c have included similar grain-sized material. The coarser, low metal content OFFSHORE and CHANNEL sediments gave similar curves with few anomalous points. The INSHORE data, with mostly silt and clay-sized materials gave a scatterplot with widely spread points, a wide prediction interval, and several anomalous points.

When data from all sites are plotted on the same graph (Figure 4d), less satisfactory results are obtained. One obvious difference is that the 95% prediction band has been compressed. The large number of OFFSHORE and CHANNEL samples that plot together near the ordinant along the x-axis had the effect of compressing the confidence band. Even so, only three additional samples fall above the line as being described as having anomalously high Cu values.

As a more direct test of the influence of particle size on the metal/Fe plots, samples for which particle size analysis had been conducted were selected. Figure 6a shows plots of Zn vs Fe for all data available and only for those samples having >15% clay (Figure 6b). Because of the nature of the study area sediments, most of these data are from the INSHORE sites. The INSHORE data are shown in Figure 6c). The plot of Zn vs Fe for >15% clay samples gives a regression line and 95% prediction interval which fit the data much better than for the plot of all data. Plots for other metals when grouped according to clay or silt and clay content were similar to that in Figure 5. The more narrow confidence band is again evident in the all data plot. It appears that the potential difficulty with the all data plots is with the great number of data points (from OFFSHORE and CHANNEL)

lying together near the ordinant and not with the particle-size difference. Improved evaluation of the lower concentration samples (OFFSHORE and CHANNEL sands) can be better accomplished by plotting them separately or as one group (Figure 5b) but evaluation of the INSHORE data set was affected only slightly by the all data plot.

Another method for assessing geochemical data is the enrichment factor, EF (Zoller *et al.*, 1974; Sinex and Helz, 1981). The EF is defined for this data analysis as:

$$EF = \frac{(X/Fe) \text{ sediment}}{(X/Fe) \text{ Earth's crust}}$$

where X/Fe is the ratio of the concentration of element X to Fe. Anthropogenic inputs of Fe are relatively small as compared to natural sources (Helz, 1976) so Fe was chosen as the element for normalization. Aluminum is also used as the element for normalization (Zoller *et al.*, 1974; Helz *et al.*, 1983) and thought by these workers to perhaps be more desirable than Fe. Since Al data were not available for all sediments in the current study, Fe and Al could not be compared, nor Al used. For the samples where both Fe and Al analysis were available, plots of Fe vs Al gave a correlation of 0.90 (Figure 6d).

The major assumption, or perhaps limitation, of this method is the use of average crustal abundance data. A study area may be either enriched or depleted in relation to the average crustal abundance and still be free of anthropogenic inputs. This method does, however, give a common reference point for comparison. A value of 1 would mean neither enrichment

nor depletion in relation to the Earth's crust. The crustal abundance data of Taylor (1964) were used to compute the EF for all data in this paper. Sinex and Helz (1981) state that the EF is not very sensitive to the choice of reference material and if average shale data were used instead of average crustal abundance, the enrichment factors would change by less than 10% except for Cd, Pb, and Zn which would decrease ~40-50%.

Enrichment factors for metals from the study area sediments are shown in Table 5. The enrichment factors were computed for individual samples within each location group and then individual EFs were averaged to obtain the group value. Elements that show definite enrichment are Cd, Cu, Pb, and Zn. The greatest enrichment occurs, as expected, in the heavily industrialized Elizabeth River. Cadmium and Pb show the greatest enrichment with Zn next and the least for Cu. The enrichment patterns for these four elements are similar; almost identical for Cu, Pb, and Zn, and slightly different for Cd. The seemingly high enrichment factors for Cd and Pb for the OFFSHORE and Thimble channel sediments are probably because of the relatively low concentrations for Fe. Cadmium and Pb concentrations in these sediments were very low; several will have to be reanalyzed with larger aliquots to give values above detection limits. Given the nature of the sediments (sands) and the very low Fe values, these enrichment factors should be cautiously interpreted. Even though the OFFSHORE samples are defined as being enriched, the absolute concentrations of Cd and Pb obviously indicate no need for environmental concern. The enrichment factors for Cd, Cu, Pb, and Zn are within the range of values computed by Sinex and Helz (1981) for various East and Gulf Coast estuaries. Enrichment factors for Co, Cr, Mn, and Ni were at or below one.

Mean enrichment factors from the data comparison with Johnson and Villa, Jr. (1976) are presented in Table 6. Strong enrichment of Cd, Pb, and Zn is evident in both sets of data. However, there was an apparent decrease in the enrichment factor for Cd from 1974 to 1979 in the lower portion (Main Stem). This decrease most likely resulted from reduced input of wastes and wastewater from a chemical plant along the river. Factors for Cr are unity (or near) in all cases and there has been no change for Cu, Pb, or Zn since 1974.

### Summary and Conclusions

The mean concentrations for extractable sediment metals were evaluated with respect to average crustal abundances. Levels of Cd, Cu, Pb, and Zn exceeded average crustal abundances for most of the study sites. Mean values for Cd, Cr, Cu, Fe, Pb, and Zn were not statistically different from samples measured in 1974 in the Elizabeth River. The range of values for the current study was much more narrow than in 1974.

Cumulative frequency curves suggested that there were two major populations for all metals and perhaps a third and smaller one for Cd, Cr, and Mn.

Plots of metal vs Fe indicated that sediments from the NDS site and The Thimble Shoal Channel were not anthropogenically affected and, for most metals, were slightly different in their geochemical nature. These plots for INSHORE data were very different and indicated that several sites were enriched well above natural levels. Grouping of sediments as a function

of particle size gave less scatter of the points and identified anomalously high samples. Based on the present results, segregation of samples based on general particle size (i.e., sand or silt and clay) before constructing metal vs Fe plots is recommended.

When the data were evaluated using the enrichment factor (EF), Cd, Cu Pb, and Zn showed enrichment with respect to crustal abundances. Because of the very low Cd and Fe values for the NDS area which resulted in high EFs, it is recommended that both sample concentrations and EF data be presented in geochemical studies.

Both the metal vs Fe plots and the EF identified anomalous metal concentrations. The metal vs Fe plots identified anomalous concentrations for a greater number of elements than did the EF. One advantage of the metal vs Fe plots is that they do not rely on average abundance data which may not be appropriate for the study area sediment.

Metal concentrations, metal vs Fe plots and enrichment factors all identified the same sections of the study area as most affected by anthropogenic sources. Each of these means of data evaluation contributes unique and useful information and all should be included in data evaluation.

A suggested approach to geochemical data analysis is to: (1) evaluate metal concentrations using appropriate crustal abundances; (2) construct cumulative frequency plots; (3) construct metal vs Fe plots utilizing particle size grouping; and/or (4) calculate enrichment factors choosing appropriate reference data. In all instances, the metal concentrations as well as plots or enrichment factors should be presented.

Metal concentration values from this and other studies (such as Sinex and Helz, 1981) are obtained from partial sediment extractions while the crustal abundances reflect total values for a given rock material. It should be noted that the EFs so calculated are conservative estimates and may actually be greater than the calculated values. Interpretation of the EFs must, therefore, be made with the type of extraction in mind and may vary from study to study. Interpretation of the results based on the extraction method can lead to estimation of the potential environmental impact based on enrichment of a given metal.

## Literature Cited

- Chester, R. and F.G. Voutsinou, 1981. The initial assessment of trace metal pollution in coastal sediments. *Marine Poll. Bull.* 12(3):84-91.
- Goldberg, E.D., V. Hodge, M. Koide, J. Griffin, E. Gamble, O.P. Bricker, G. Matisoff, G.R. Holden, Jr., and R. Braum, 1978. A pollution history of the Chesapeake Bay. *Geochim. Cosmochim. Acta.* 42:1413-1425.
- Helz, G.R., S.A. Sinex, G.H. Setlock, and A.Y. Cantillo, 1983. Chesapeake Bay study trace elements. EPA-600/3-83-012. U.S. Environmental Protection Agency, Annapolis, MD.
- Johnson, P.G. and O. Villa, Jr., 1976. Distribution of metals in the Elizabeth River. Annapolis Field Office, Tech. Report 61, Environmental Protection Agency, EPA 903/9-76-023.
- Levinson, A.A., 1980. *Introduction to Exploration Geochemistry.* Applied Publishing Ltd., Wilmette, IL.
- Nie, N.H., C.H. Hull, J.C. Jenkins, K. Steinbrenner, and D.H. Bent, 1975. *Statistical package for the social sciences.* 2nd. Ed., Eight printing, McGraw-Hill, Inc.
- Rule, J.H., 1982. Use of metal/Fe plots for detection of polluted sediments. *Abstracts for the 95th Annual Meeting of the Geological Society of America* 14(7) p. 605.
- Schrader, Jr., E.L., J.H. Rule, and W.J. Furbish, 1977. Trace metal geochemistry of a fluvial system in eastern Tennessee affected by coal mining. *Southeastern Geol.* 18(3):157-172.
- Siegel, F.R., 1974. *Applied Geochemistry.* Wiley-Interscience, John Wiley & Sons. New York.
- Sinex, S.A. and G.R. Helz, 1981. Regional geochemistry of trace elements in Chesapeake Bay sediments. *Environ. Geol.* 3:315-323.
- Sommer, S.E. and A.J. Pyzik, 1974. Geochemistry of middle Chesapeake Bay sediments from Upper Cretaceous to present. *Chesapeake Sci.* 15:39-44.
- Taylor, S.R., 1964. The abundance of chemical elements in the continental crust - a new table. *Geochim. Cosmochim. Acta.* 28:1273-1285.
- Trefry, J.H. and B.J. Presley, 1976a. Heavy metals in sediments from San Antonio Bay and the Northwest Gulf of Mexico. *Environ. Geol.* 1:283-294.

Trefry, J.H. and J.B. Presley, 1976b. Heavy metal transport from the Mississippi River to the Gulf of Mexico. In Marine Pollutant Transfer, Windom, H.L. and Ducy, R.A., eds. D.C. Heath & Co. pp.39-76.

Zoller, W.H., E.S. Gladney, G.E. Gordon, and J.J. Bors, 1974. Emissions of trace elements from coal fired power plants. In Hemphill, D.D., ed., Trace substances in environmental health 8:167-172. University of Missouri-Columbia.

TABLE I. Mean concentrations for sediment metals (mg/kg except Fe which is %).

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
NORFOLK DISPOSAL SITE	.07+ .051	3.4 +1.9	6.7+ 3.6	1.1+ .8	.559+ .228	83+ 41	4.1+ 2.1	2.7+ 1.7	15+ 7
THIMBLE CHANNEL-OUTER	.14+ .08	3.12+2.7	4.3+ 4.8	1.5+ 1.0	.606+ .295	65+ 50	5.2+ 3.0	6.6+ 1.5	14+ 7
THIMBLE CHANNEL-INNER	.27+ .12	4.86+3.7	5.3+ 6.6	4.3+ 3.6	1.05 + .563	101+ 75	9.5+ 5.2	11 + 5.6	33+ 22
NEWPORT NEWS CHANNEL	.44+ .23	7.8 +2.7	12.9+11.6	6.2+ 4.0	1.39 + .710	123+ 84	8.1+ 9.0	15 + 7	44+ 24
INNER HAMPTON ROADS	.91+ .30	16.6 +3.7	50.1+ 7.3	35.6+ 8.7	3.47 + .371	623+180	58 +15	53 +11	207+ 54
LOWER ELIZABETH RIVER (MAIN)	2.00+1.11	15.5 +5.2	52.6+ 6.6	75.4+36.5	3.62 + .551	398+ 87	43 +15	93 +39	459+197
MID-ELIZABETH RIVER	2.75+1.86	11.6 +4.7	56.4+22.7	142.1+80.0	3.16 +1.25	251+111	29 +11	157 +79	413+242
UPPER ELIZABETH RIVER	1.18+ .51	9.7 +4.0	43.9+16.5	70.8+55.0	2.39 + .982	157+ 82	38 +22	89 +53	196+103

<sup>1</sup> Ranges are +1 Standard Deviation

TABLE 2. Site legend and description of sediment type.

AREA	SITES INCLUDED	# OF SAMPLES	SEDIMENT TYPE
NORFOLK DISPOSAL SITE	Numbered Sites	49	fine sands
THIMBLE CHANNEL-OUTER	AA thru EE,U	35	coarse sands
THIMBLE CHANNEL-INNER	FF thru II,V,A	26	coarse/fine sands;silts
NEWPORT NEWS CHANNEL	B,C,D	13	silts/clays;sands;shell
INNER HAMPTON ROADS	E,F	9	silts/clays
LOWER ELIZABETH RIVER (MAIN)	G,H,I	12	clays/silts
MID-ELIZABETH RIVER	K,L,M	12	clays/silts
UPPER ELIZABETH RIVER	P,Q,S,T	16	clays/silts

TABLE 3. Average crustal abundance data from Taylor (1964).

ELEMENT:	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
μg/g:	0.2	25	100	55	5.63%	950	75	12.5	70

TABLE 4. Means and standard deviations of trace metals in Elizabeth River sediments from the current study and from Johnson and Villa, Jr. (1976)<sup>1</sup>.

METAL (mg/kg)	MAIN STEM		SOUTHERN BRANCH	
	1974, EPA <sup>2</sup>	1979, RULE <sup>2</sup>	1974, EPA <sup>2</sup>	1979, RULE <sup>2</sup>
Cd	5.3 <u>+5.5</u>	2.0 <u>+1.1</u>	2.3 <u>+1.6</u>	2.3 <u>+1.6</u>
Cr	47 <u>+26</u>	52 <u>+6.6</u>	40 <u>+30</u>	57 <u>+17</u>
Cu	38 <u>+43</u>	75 <u>+36</u>	82 <u>+91</u>	130 <u>+69</u>
Fe	28834 <u>+8043</u>	36208 <u>+5512</u>	25092 <u>+8145</u>	31825 <u>+9736</u>
Pb	70 <u>+68</u>	93 <u>+39</u>	106 <u>+101</u>	149 <u>+62</u>
Zn	386 <u>+404</u>	459 <u>+197</u>	287 <u>+263</u>	363 <u>+197</u>

<sup>1</sup>Sites were chosen from the current study to correspond with the areas sampled by Johnson and Villa, Jr. (1976).

<sup>2</sup>Sampling for the Johnson and Villa, Jr. study was conducted in 1974, and in the Elizabeth River for the current study in 1979.

TABLE 5. Mean enrichment factors for sediments of the study areas<sup>1</sup>.

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
NORFOLK DISPOSAL SITE	5.9 $\pm$ 6.6 <sup>2</sup>	1.4 $\pm$ 1.0	0.7 $\pm$ 0.2	0.2 $\pm$ 0.1	0.8 $\pm$ 0.2	0.6 $\pm$ 0.2	2.5 $\pm$ 2.3	2.0 $\pm$ 0.6
THIMBLE CHANNEL-OUTER	6.1 $\pm$ 4.0	1.8 $\pm$ 0.9	0.4 $\pm$ 0.2	0.3 $\pm$ 0.1	0.7 $\pm$ 0.7	0.6 $\pm$ 0.2	5.1 $\pm$ 1.8	1.9 $\pm$ 0.5
THIMBLE CHANNEL-INNER	7.3 $\pm$ 2.4	1.2 $\pm$ 0.3	0.4 $\pm$ 0.3	0.4 $\pm$ 0.2	0.5 $\pm$ 0.2	0.7 $\pm$ 0.2	4.9 $\pm$ 1.8	2.4 $\pm$ 0.5
NEWPORT NEWS CHANNEL	10.0 $\pm$ 6.0	1.3 $\pm$ 0.3	0.5 $\pm$ 0.3	0.5 $\pm$ 0.2	0.5 $\pm$ 0.2	0.4 $\pm$ 0.3	5.2 $\pm$ 2.4	2.6 $\pm$ 0.9
INNER HAMPTON ROADS	7.3 $\pm$ 1.9	1.1 $\pm$ 0.2	0.8 $\pm$ 0.1	1.0 $\pm$ 0.2	1.0 $\pm$ 0.2	1.2 $\pm$ 0.2	6.8 $\pm$ 0.8	4.7 $\pm$ 0.8
LOWER ELIZABETH RIVER (MAIN)	15.0 $\pm$ 7.9	1.0 $\pm$ 0.3	0.8 $\pm$ 0.1	2.3 $\pm$ 1.4	0.7 $\pm$ 0.1	0.9 $\pm$ 0.4	11.6 $\pm$ 4.2	9.9 $\pm$ 3.2
MID-ELIZABETH RIVER	22.9 $\pm$ 10.4	0.8 $\pm$ 0.2	1.0 $\pm$ 0.1	4.3 $\pm$ 1.3	0.5 $\pm$ 0.0	0.7 $\pm$ 0.0	21.1 $\pm$ 4.6	9.7 $\pm$ 3.3
UPPER ELIZABETH	14.5 $\pm$ 3.6	0.9 $\pm$ 0.2	1.1 $\pm$ 0.4	2.7 $\pm$ 1.3	0.4 $\pm$ 0.1	1.2 $\pm$ 0.4	15.8 $\pm$ 1.7	6.4 $\pm$ 1.2

<sup>1</sup>Enrichment factors (E.F.) were calculated for individual samples in each location area and an average E.F. for the area then calculated.

<sup>2</sup>Ranges are  $\pm$  Standard Deviation.

TABLE 6. Comparison of enrichment factors from the current data with that from Johnson & Villa, Jr. (1976) for the Elizabeth River.

METAL	MAIN STEM		SOUTHERN BRANCH	
	1974, EPA	1979, RULE	1974, EPA	1979, RULE
Cd	59 <u>+74</u> <sup>1</sup>	15 <u>+7.9</u>	23 <u>+12</u>	19 <u>+9.4</u>
Cr	1.0 <u>+ 0.9</u>	0.8 <u>+0.1</u>	0.8 <u>+ 0.4</u>	1.0 <u>+0.1</u>
Cu	1.4 <u>+ 1.5</u>	2.3 <u>+1.4</u>	3.1 <u>+ 2.7</u>	4.0 <u>+1.3</u>
Pb	12 <u>+12</u>	12 <u>+4.2</u>	18 <u>+14</u>	21 <u>+4.0</u>
Zn	11 <u>+11</u>	10 <u>+3.2</u>	9 <u>+ 6</u>	8 <u>+2.9</u>

<sup>1</sup>Ranges are + Standard Deviation.

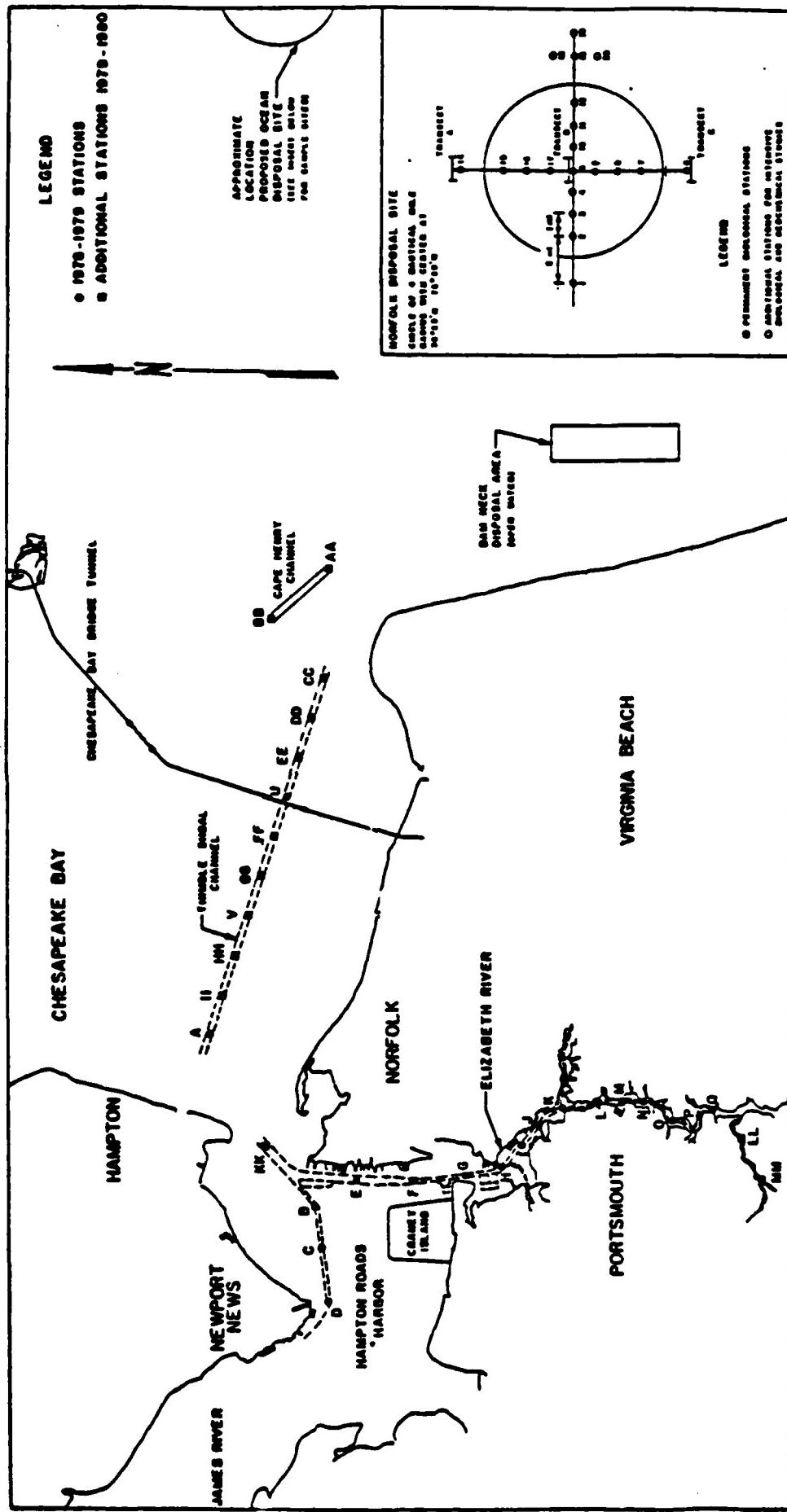


FIGURE 1. Study Area.

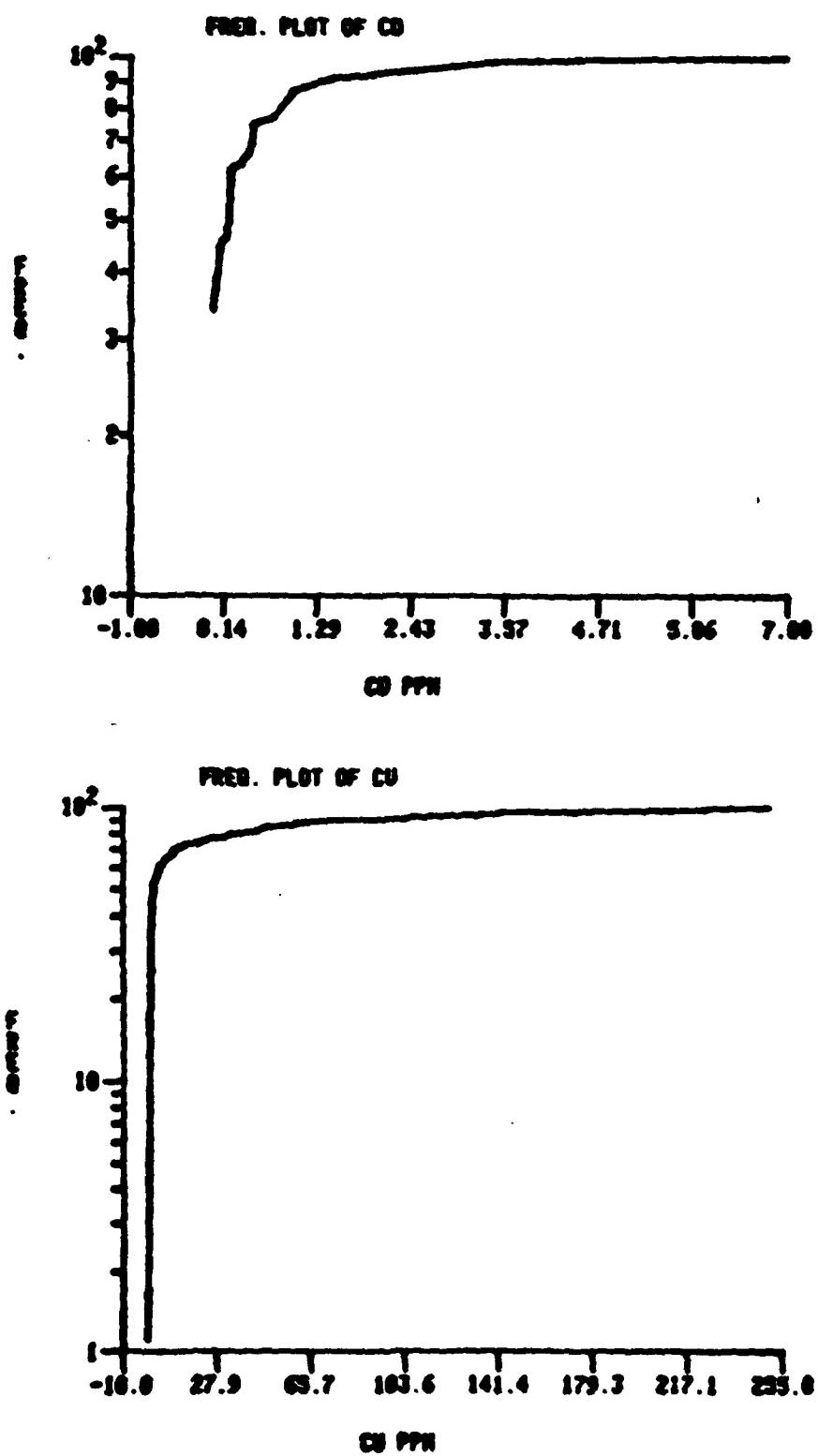


FIGURE 2. Cumulative frequency curves for Cd and Cu.

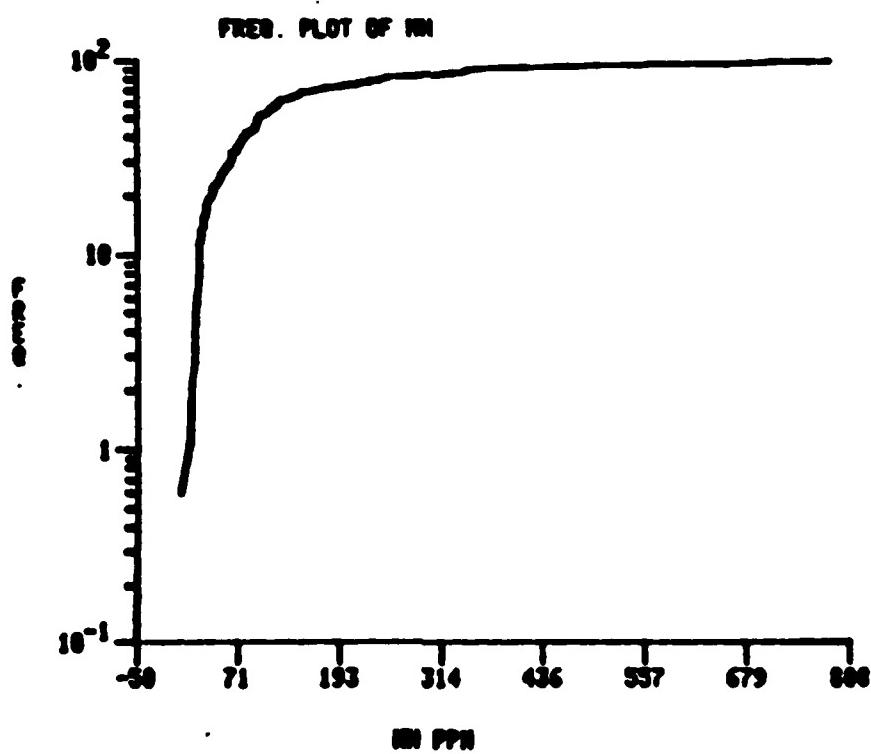
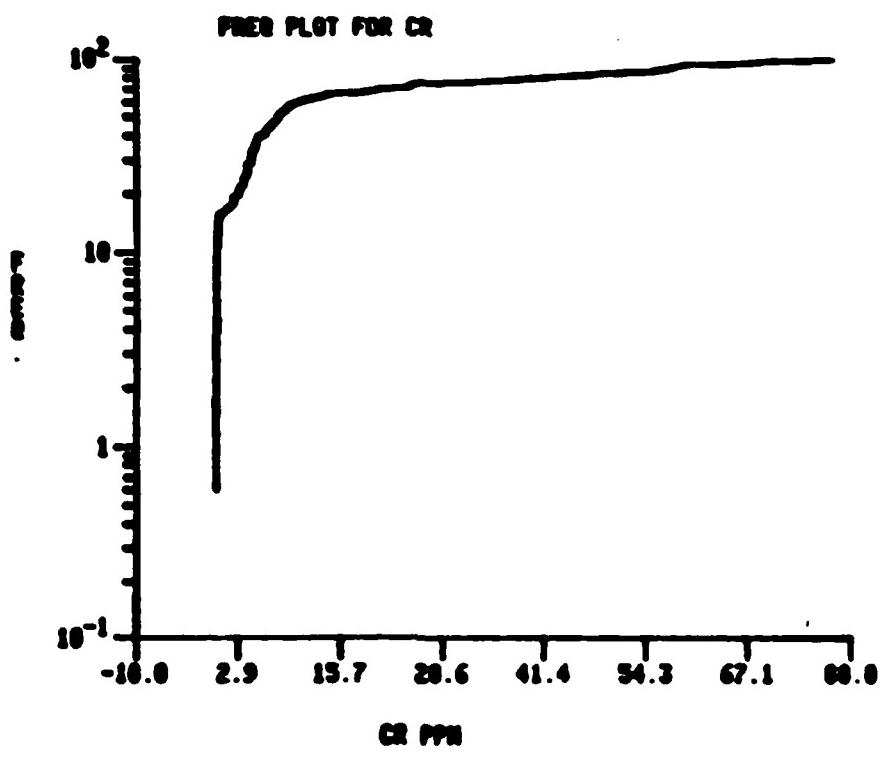


FIGURE 3. Cumulative frequency curves for Cr and Mn.

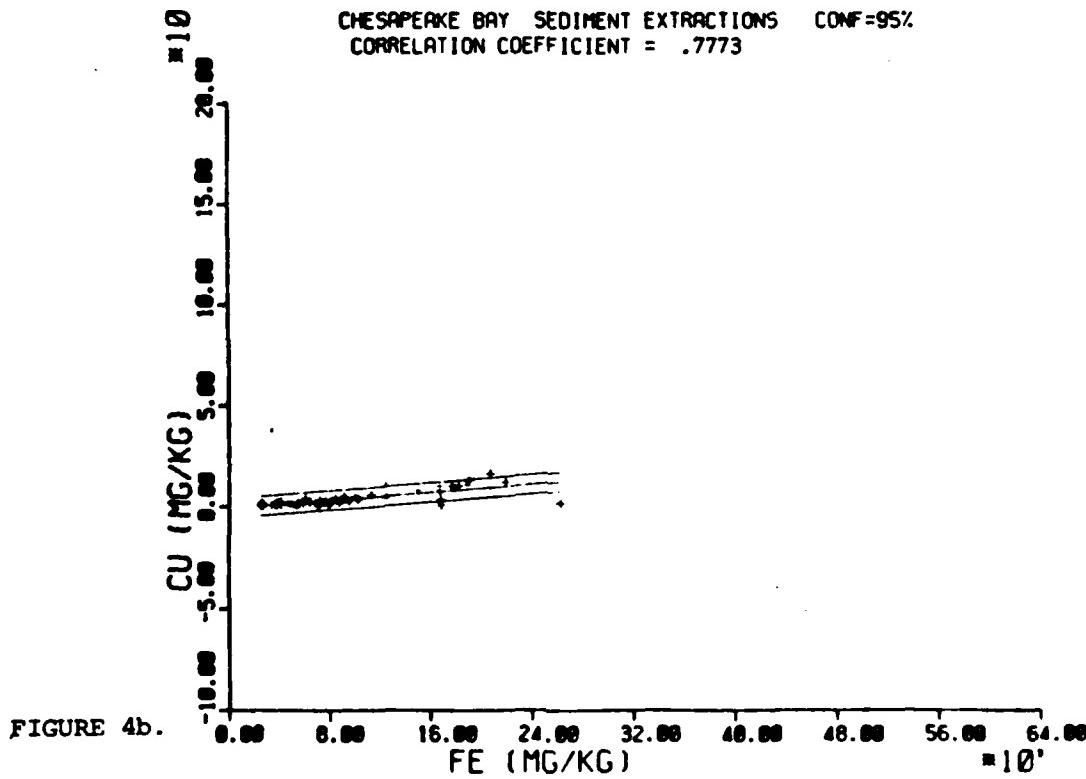
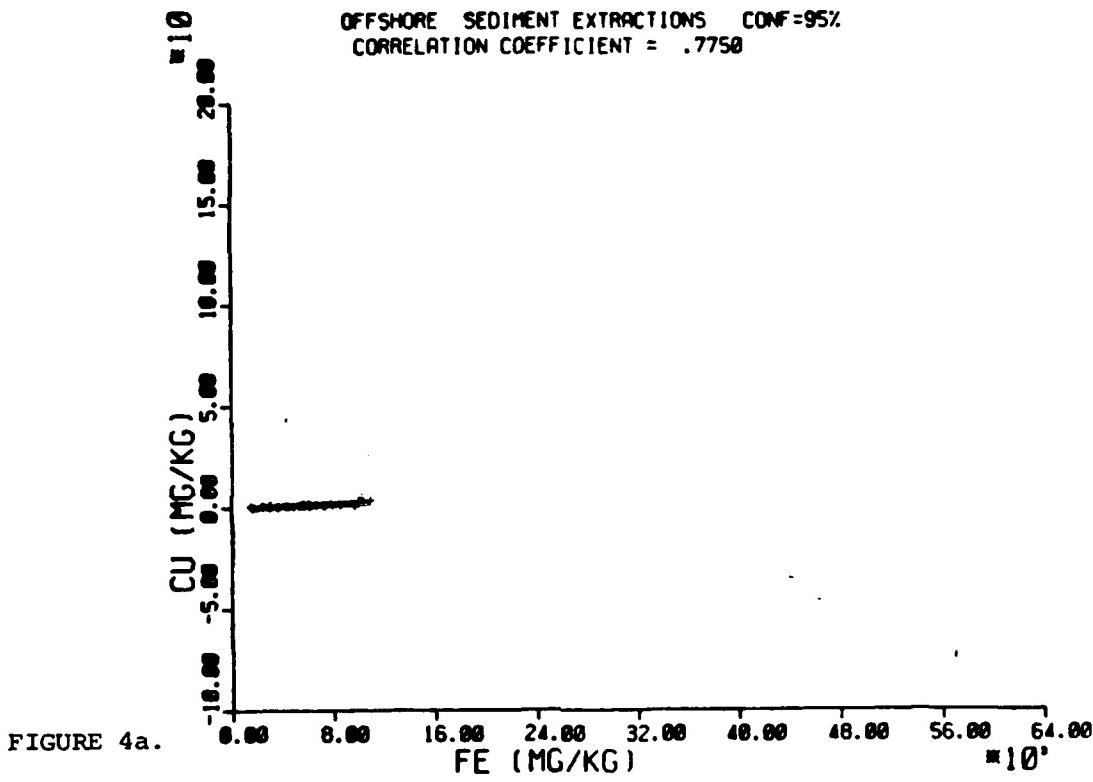


FIGURE 4. Scatterplots for Cu vs Fe with the 95% prediction interval.

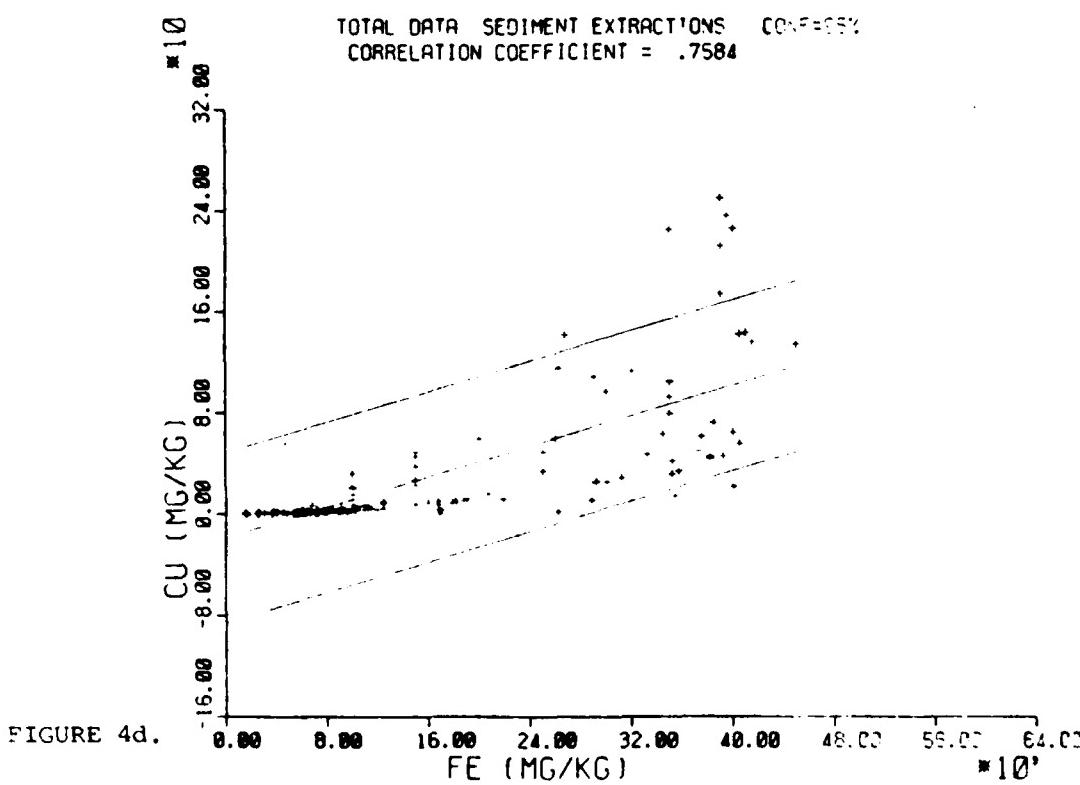
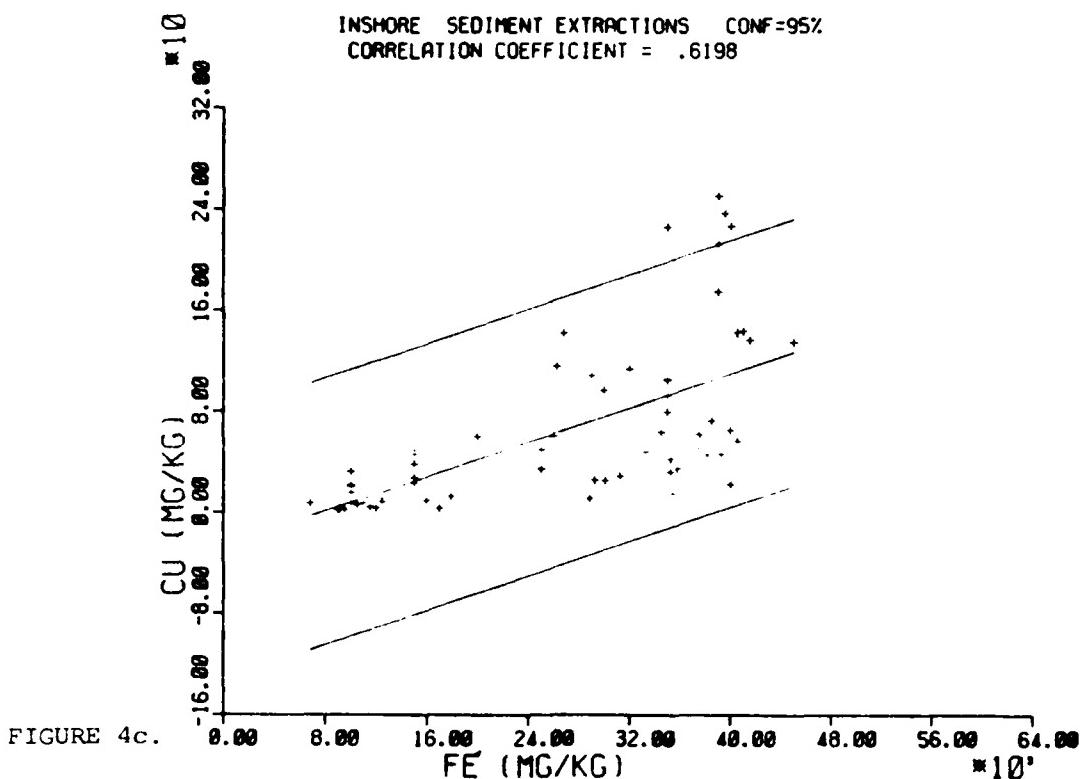
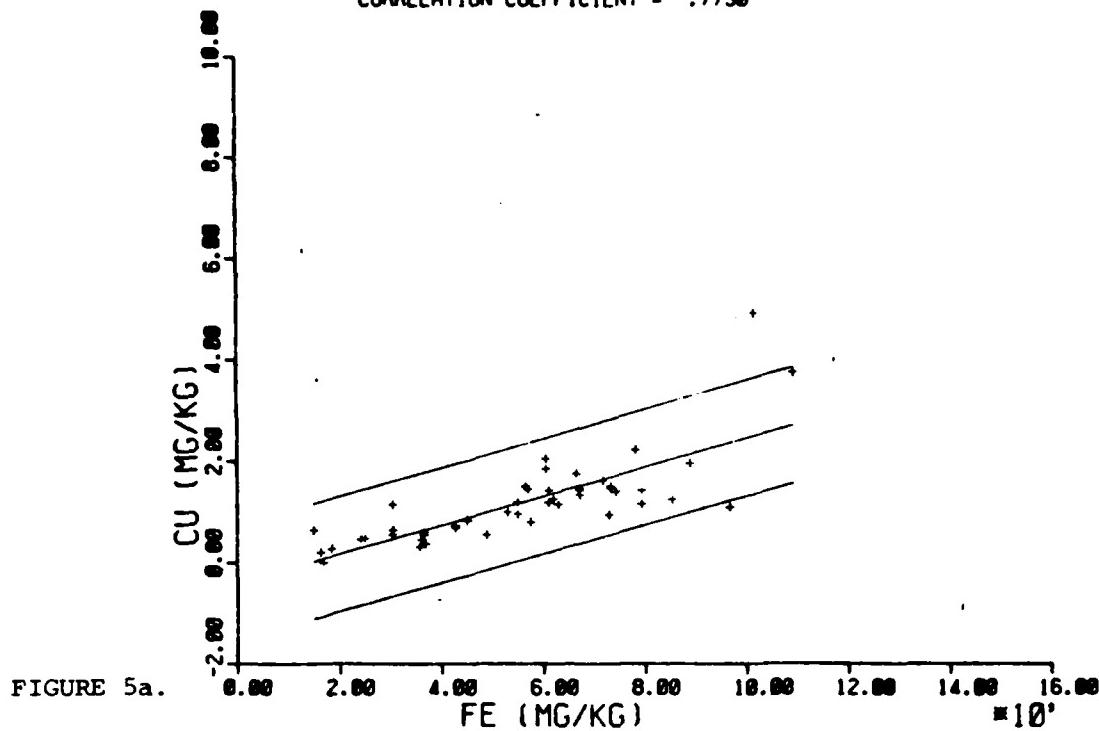


FIGURE 4. concluded.

OFFSHORE SEDIMENT EXTRACTIONS CONF=95%  
CORRELATION COEFFICIENT = .7750



CHESAPEAKE BAY SEDIMENT EXTRACTIONS CONF=95%  
CORRELATION COEFFICIENT = .2790

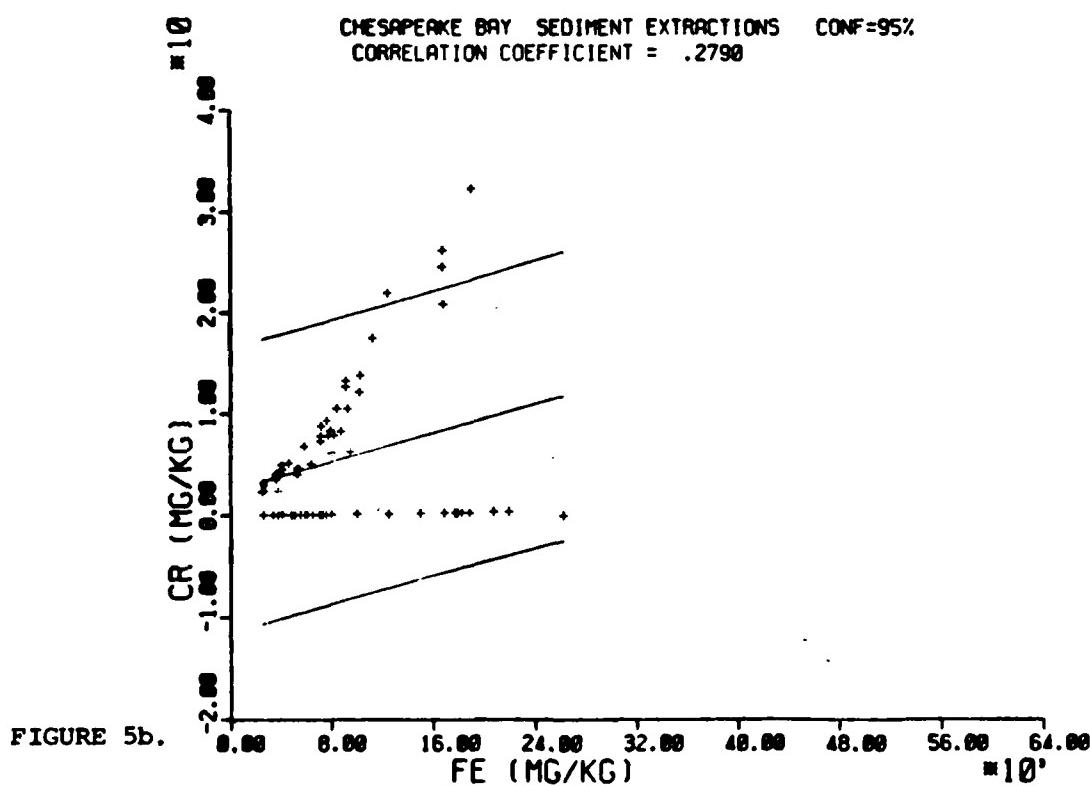


FIGURE 5. Scatterplots for Cu vs Fe and Cr vs Fe with the 95% prediction interval.

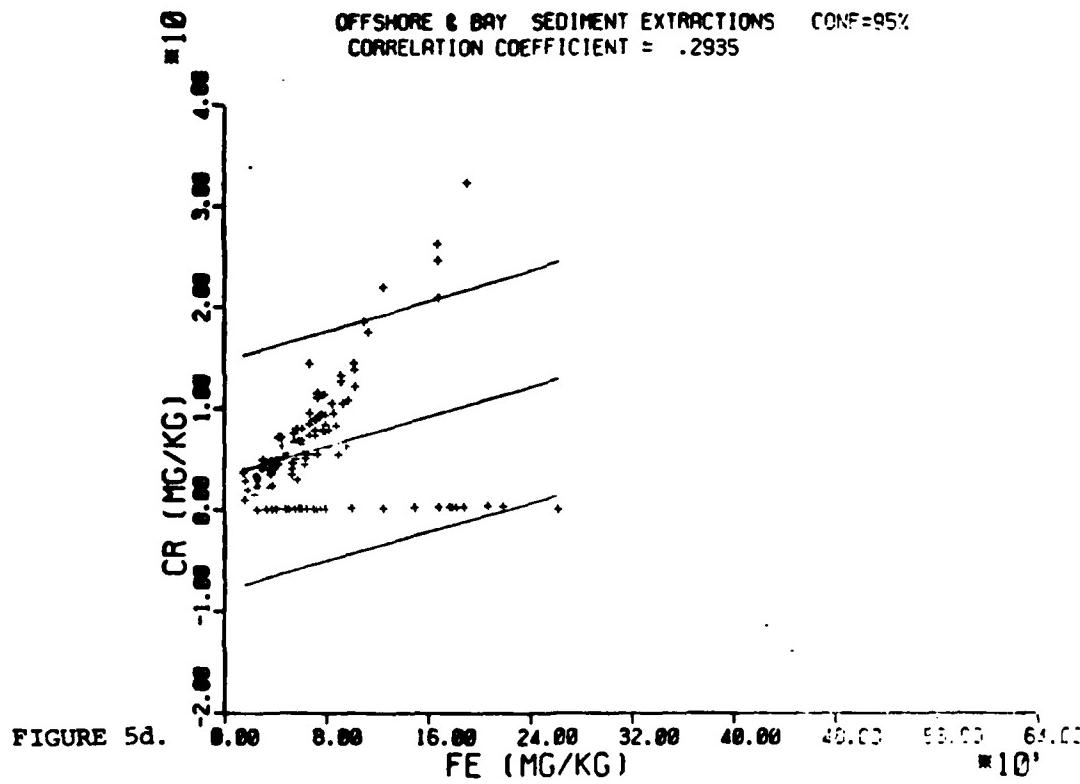
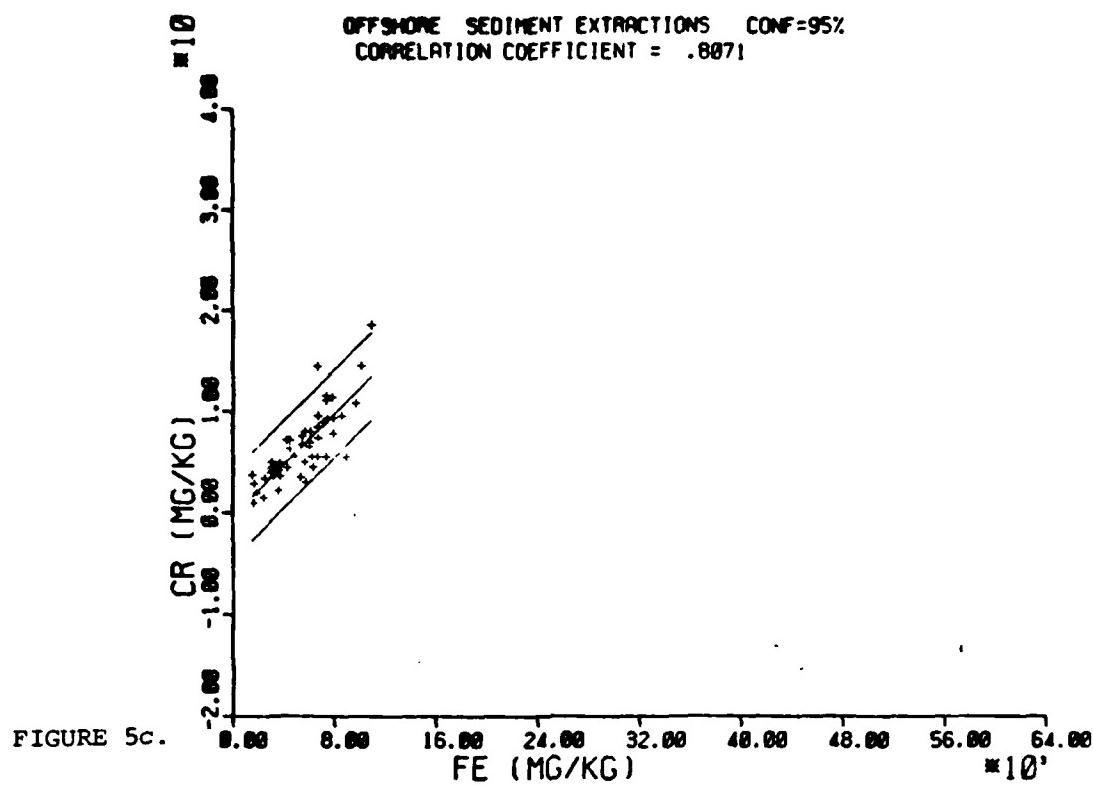


FIGURE 5. concluded.

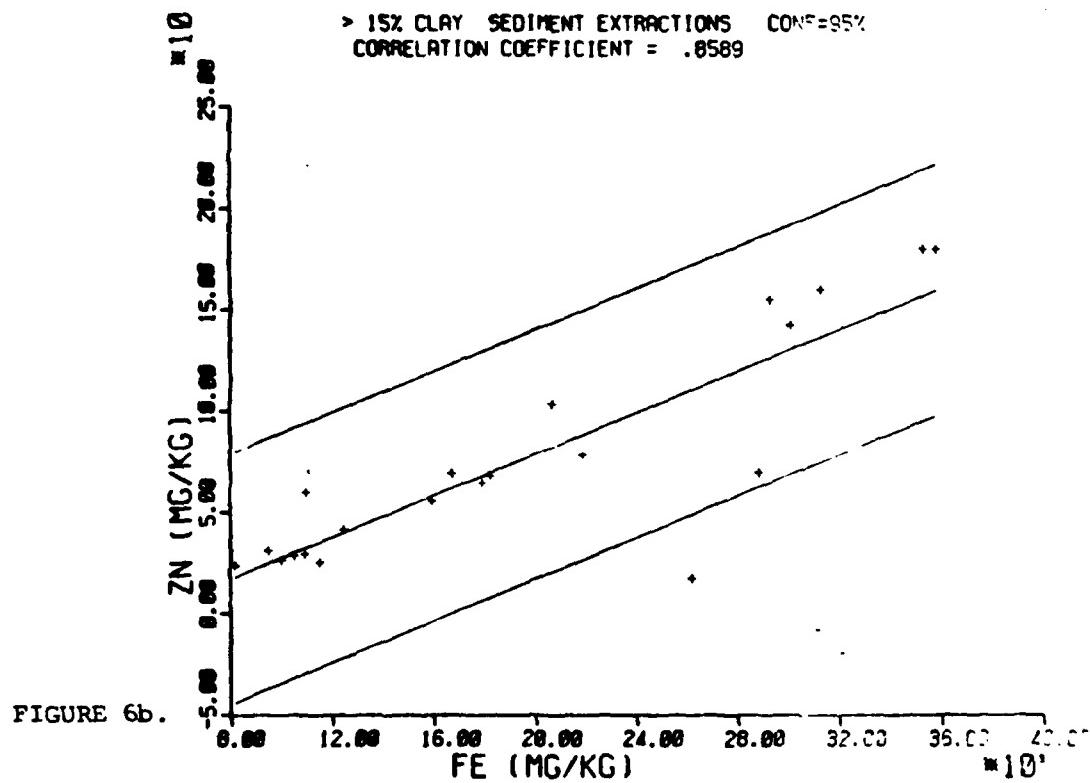
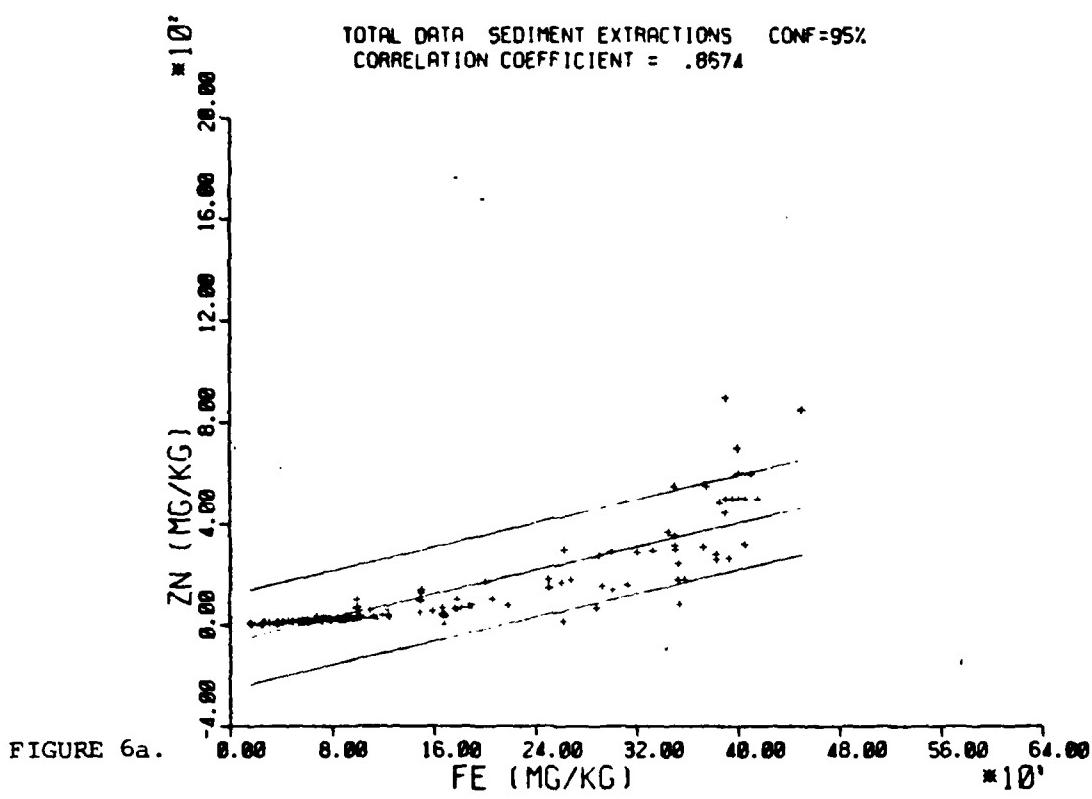


FIGURE 6. Scatterplots for Zn vs Fe and Al vs Fe with the 95% prediction interval.

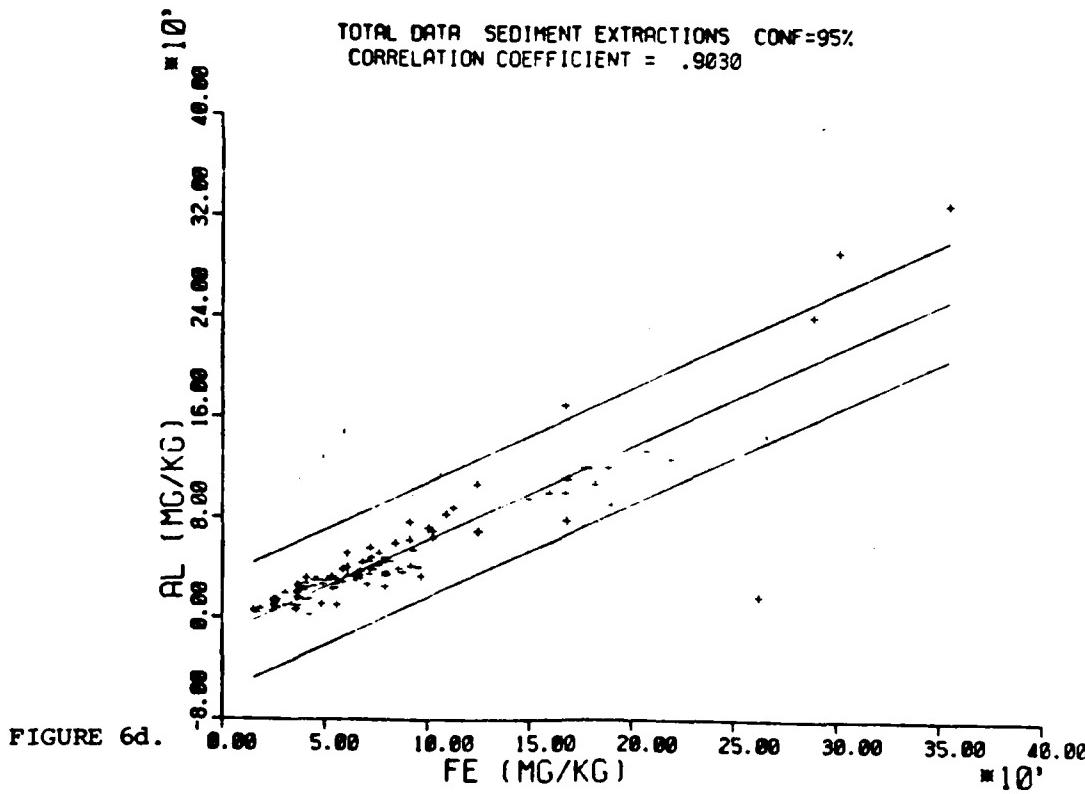
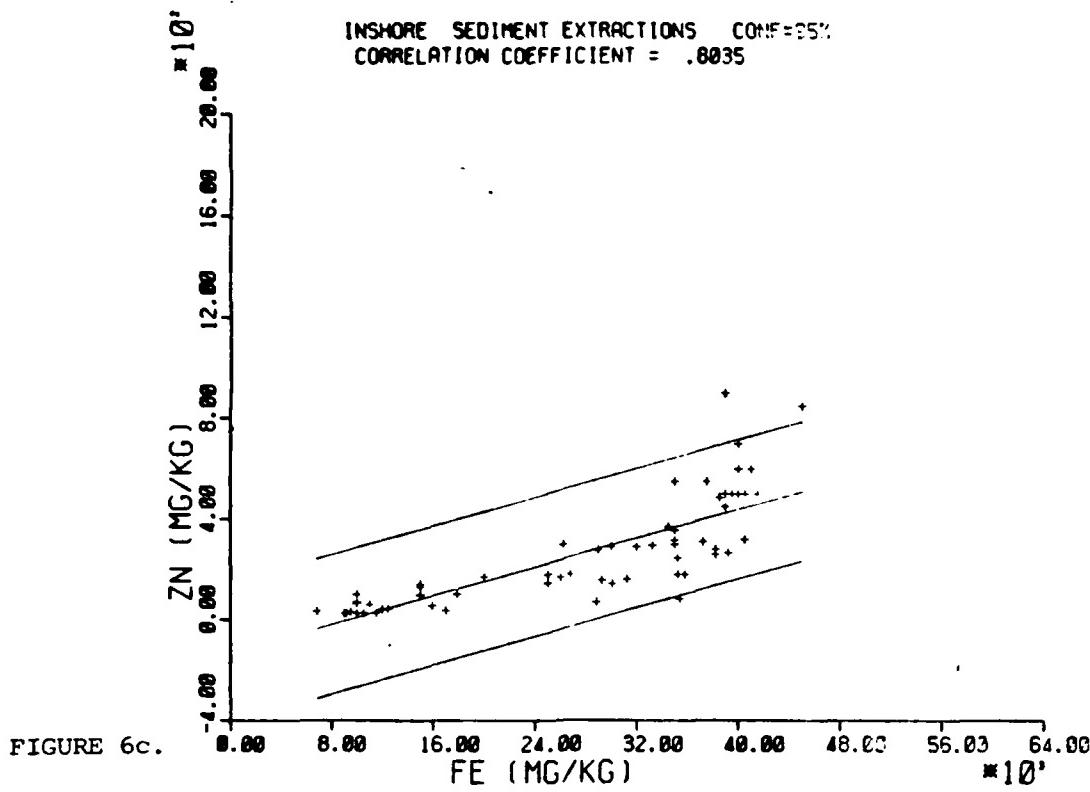


FIGURE 6. concluded.

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